PROCESS FOR PREPARING AN ALKALI METAL

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ABSTRACT

Process for preparing an alkali metal from a salt of the alkali metal which is soluble in a solvent, including a first electrolysis, a concentration, and a second electrolysis. The first electrolysis produces a product mixture. This product mixture is then concentrated to give a largely solvent-free alkali metal (poly)sulfide melt. A second electrolysis at a temperature above the melting point of the alkali metal is then performed in a second electrolysis cell comprising an anode space and a cathode space, separated by a solid electrolyte which conducts alkali metal cations. The alkali metal (poly)sulfide melt from the concentration step is fed to the anode space. Sulfur is removed from the anode space and liquid alkali metal is removed from the cathode space.
FIG. 2
FIG. 4


**PROCESS FOR PREPARING AN ALKALI METAL**

[0001] The invention relates to a process for preparing an alkali metal from a salt of the alkali metal which is soluble in a solvent.

[0002] Alkali metals, which are used as important basic inorganic chemicals, are, in particular, lithium, potassium and sodium. Thus, lithium is used, for example, for the preparation of organolithium compounds, as alloying additive to aluminum or magnesium and for lithium batteries. Lithium is prepared industrially by melt flux electrolysis of a eutectic mixture of lithium chloride and potassium chloride at from 400 to 460°C. However, this process has a high energy consumption. In addition, the process has the serious disadvantage that only water-free lithium chloride can be used. The lithium chloride which is initially present as aqueous solution therefore has to be worked up to give the water-free solid in an energy-intensive process. Since lithium chloride is hygroscopic, drying and handling requires particular precautions.

[0003] When carrying out organolithium reactions, aqueous lithium salt solutions are frequently obtained. As a result of the increasing demand for lithium batteries, lithium-containing waste is also obtained there. This too, can be converted into aqueous lithium salt solutions. Since lithium is also very expensive in the form of its salts, recycling of lithium is of interest.

[0004] Sodium is used, for example, for the preparation of sodium amide, sodium alkoxides and sodium borohydride. Sodium is obtained industrially by the Downs process by electrolysis of molten sodium chloride. This process has a high energy consumption of more than 10 kWh/kg of sodium. Furthermore, the process has the serious disadvantage that the electrolysis cells are destroyed by solidification of the salt melt when they are switched off. Furthermore, the sodium metal obtained by the Downs process has the disadvantage that it is, owing to the process, contaminated with calcium whose residual content can only be reduced but never completely eliminated by means of subsequent purification steps.

[0005] Potassium is used, for example, for the preparation of potassium alkoxides, potassium amides and potassium aldehydes. At present, potassium is obtained industrially mainly by reduction of potassium chloride by means of sodium. This firstly forms the sodium-potassium alloy NaK which is subsequently fractionally distilled. A good yield is obtained by potassium vapor continually being taken off from the reaction zone, as a result of which the equilibrium of the reaction is shifted to the potassium side. However, this process operates at high temperatures of about 870°C. In addition, the potassium formed comprises about 1% of sodium as impurity and therefore has to be purified by means of a further rectification. However, the greatest disadvantage is that the sodium used is expensive since it has to be obtained industrially by the Downs process by electrolysis of molten sodium chloride.

[0006] An alternative process for isolating an alkali metal from aqueous solution is described in WO 01/14616 A1. For this purpose, an aqueous solution of an alkali metal salt is fed to an electrolysis cell which has a cathode compartment and an anode compartment which are separated from one another by a solid electrolyte. The solid electrolyte has at least one further ion-conducting layer. The cathode compartment has a solid cathode core and is filled with a fusible alkali metal or a liquid electrolyte. The alkali metal is formed on the cathode and ascends in the liquid electrolyte and can then be taken off. Preference is given to using salt melts of the alkali metal to be isolated as liquid electrolyte. The disadvantage of the process is the increased electrical resistance and the unsatisfactory stability of the combination of solid electrolytes and the further ion-conducting layer.

[0007] A further alternative process for preparing sodium as alkali metal is described in DE 195 33 214 A1. Here, an electrolyte comprising essentially sodium tetrachloroaluminate is electrolyzed in an anode space of an electrolysis cell, with aluminum chloride formed being given off as vapor and sodium being passed through a solid electrolyte which conducts sodium ions and taken off from the cathode space. The disadvantage of this process is the coupled production of aluminum chloride and sodium, when there is not the same demand for the products.

[0008] It is an object of the present invention to provide a process for preparing an alkali metal, which firstly does not have the disadvantages known from the prior art, especially has a lower energy consumption and is less complicated to operate in terms of apparatus.

[0009] The object is achieved by a process for preparing an alkali metal from a salt of the alkali metal which is soluble in a solvent, which comprises the following steps:

[0010] (a) carrying out of a first electrolysis in a first electrolysis cell comprising an anode space and a cathode space, where the anode space and the cathode space of the first electrolysis cell are separated by a membrane which is permeable to alkali metal cations, where the salt of the alkali metal dissolved in the solvent is fed to the anode space and a suspension comprising sulfur and a second solvent is fed to the cathode space and a mixture comprising the second solvent, alkali metal cations, (poly)sulfide anions and anions of oxygen-sulfur compounds is taken off from the cathode space,

[0011] (b) concentration of the mixture comprising second solvent, alkali metal cations, (poly)sulfide anions and anions of oxygen-sulfur compounds which is taken off from the cathode space to give a largely solvent-free alkali metal (poly)sulfide melt,

[0012] (c) carrying out of a second electrolysis at a temperature above the melting point of the alkali metal in a second electrolysis cell comprising an anode space and a cathode space, where the anode space and the cathode space of the second electrolysis cell are separated by a solid electrolyte which conducts alkali metal cations and the alkali metal (poly)sulfide melt from step (b) is fed to the anode space and sulfur and unreacted alkali metal (poly)sulfide melt are taken off from the anode space and liquid alkali metal is taken off from the cathode space.

[0013] The process of the invention is suitable for preparing an essentially pure alkali metal, in particular for the preparation of sodium, potassium and lithium, very particularly preferably for the preparation of sodium.

[0014] For the purposes of the present invention, essentially pure means that the proportion of foreign metal impurities in the alkali metal is not more than 30 ppm.

[0015] For the purposes of the present invention, (poly)sulfide anions are anions of the general formula $S_x^{2-}$, where $x$ is any integer from 1 to 6.

[0016] For the purposes of the present invention, the term alkali metal (poly)sulfide encompasses all compounds of the general formula $MeS_x$

[0017] where $Me$ is the alkali metal, for example sodium, potassium or lithium, and $x$ is any integer in the range from 1 to 6.
For the purposes of the present invention, the term largely solvent-free alkali metal (poly)sulfide melt means that the alkali metal (poly)sulfide melt comprises not more than 5% by weight of solvent, preferably not more than 3% by weight of solvent and in particular not more than 1.5% by weight of solvent.

To prepare the alkali metal, a first electrolysis is carried out in a first electrolysis cell comprising an anode space and a cathode space in the first step (a). The salt of the alkali metal dissolved in the solvent is fed to the anode space of the electrolysis cell. Alkali metal halides are particularly suitable as salt fed to the anode space of the first electrolysis cell. Very particular preference is given to using alkali metal chlorides. The solvent is for example water or an organic solvent, for example an alcohol. The solvent is preferably water. When the process is used for the preparation of sodium, an aqueous sodium chloride solution, in particular, is fed to the anode space of the first electrolysis cell.

When using an aqueous alkali metal salt solution, for example an aqueous sodium chloride solution or an aqueous potassium chloride solution, preference is given to using a solution as is also customary in chloralkali electrolysis. Before introduction into the anode space of the first electrolysis cell, the alkali metal chloride solution is usually purified in order to remove nonalkali metal ions.

When the process is used for preparing sodium and a sodium chloride solution is fed in as solution fed to the anode space, this solution preferably comprises not more than 500 ppm of potassium based on the total amount of sodium and potassium comprised in the solution.

When the process is used for preparing potassium, preference is given to using an aqueous potassium chloride solution which has likewise, as is known from chloralkali electrolysis, been purified and is free of nonalkali metal ions. The solution preferably comprises not more than 0.1% by weight of sodium, based on the total amount of potassium and sodium in the solution.

The solution of the alkali metal salt fed to the anode space of the first electrolysis cell is preferably virtually saturated and preferably comprises, for example in the case of sodium chloride, from 5 to 27% by weight, in particular from 15 to 25% by weight, for example 23% by weight, of sodium chloride.

A second solvent and sulfur powder are fed as a suspension to the cathode space of the electrolysis cell. The solution fed to the cathode space preferably additionally comprises electrolyte salts, for example alkali metal hydroxide or particularly preferably alkali metal (poly)sulfides, in order to increase the conductivity of the solution. The alkali metal of the alkali metal hydroxide or the alkali metal (poly)sulfides is preferably the same as the alkali metal to be isolated. The solution fed to the cathode space preferably comprises from 50 to 95% by weight of solvent and from 2 to 25% by weight of elemental sulfur. Furthermore, from 2 to 5% by weight of alkali metal hydroxide and from 0 to 48% by weight of alkali metal sulfur compounds are preferably comprised. Particular preference is given to the solution being circulated in continuous operation in the cathode space. Second solvent and sulfur powder are continuously introduced into the circulated solution, so that the circulated solution comprises a concentration of from 25 to 50% by weight of sulfur compounds. This is achieved by adding a suspension composed of from 50 to 82% by weight of water and from 18 to 50% by weight of sulfur powder to the circulated solution. The second solvent can be an organic solvent, for example an alcohol, or water. The second solvent is preferably water.

The anode space and the cathode space of the first electrolysis cell are separated by a membrane which is permeable to alkali metal cations and acts as a barrier to anions. Suitable membranes which are permeable to alkali metal cations are all cation-selective membranes which are permeable to alkali metal cations. Suitable cation-permeable membranes are, for example, Nation® membranes, which are commercially available. Such a membrane usually has a framework of polytetrafluoroethylene with immobilized anions, generally sulfonic acid groups and/or carboxylate groups.

The anode used is, for example, an anode as is known from chloralkali electrolysis. As regards the electrode design, it is generally possible to use perforated materials, for example in the form of meshes, lamellae, oval profile struts, V-struts or round profile struts. The anode is preferably a dimensionally stable anode which is generally made up of coated titanium, with metal mixed oxides of titanium, tantalum and/or platinum metals such as iridium, ruthenium, platinum and rhodium being used for coating. The platinum metals and the proportion of the metal are selected so as to achieve a very low overvoltage for the formation of chlorine and a very high overvoltage for oxygen. For example, the chlorine overvoltage is from 0.1 to 0.4 volt and the oxygen overvoltage is from 0.6 to 0.9 volt. Graphite is in principle also a suitable material for the anode but is generally not dimensionally stable under the operating conditions, so that the anodes made therefrom have to be adjusted and regularly replaced during operation in the cell, while in the case of titanium passivated with mixed oxides, the coating has to be replaced only after continuous operation for from 2 to 4 years.

As cathode, it is possible to use a cathode as is known from chloralkali electrolysis, for example a stainless steel cathode or a nickel electrode. In a preferred embodiment, a graphite felt is additionally introduced into the electrode gap between stainless steel cathode and membrane.

The first electrolysis is preferably carried out continuously, with the salt of the alkali metal dissolved in a solvent being fed continuously to the anode space and the aqueous sulfur suspension or the (poly)sulfide/sulfur mixture recirculated from the second electrolysis and second solvent being fed continuously to the cathode space. During the electrolysis, alkali metal cations migrate as a result of the applied current through the cation-selective membrane from the anode side to the cathode side. Chlorine is formed at the anode and is removed from the anode space. Furthermore, the solution comprising alkali metal salt is taken off from the anode space. The solution of the alkali metal salt which is taken off is, in one embodiment, dechlorinated, concentrated to feed concentration, purified and recirculated to the anode space. To concentrate the solution, it is possible, for example, to introduce alkali metal salt directly into the solution of the alkali metal salt.

A mixture of alkali metal (poly)sulfides and ionic sulfur compounds, for example sulfites, thiosulfates, is formed in the cathode space, thus giving an aqueous solution comprising alkali metal cations and ionic sulfur compounds. In addition, the solution initially comprises unreacted, undisolved elemental sulfur. The solution is taken off from the cathode space and preferably circulated in order to concentrate the product, namely the alkali metal cations and the ionic sulfur compounds. A substream is taken off from the mixture.
comprising second solvent, alkali metal cations, (poly)sulfide anions and ionic sulfur compounds which is taken off from the cathode space and concentrated in step (b).  

[0030] The electrolysis in step (a) is preferably carried out at a temperature in the range from 25 to 120°C, preferably in the range from 50 to 90°C, and in particular in the range from 75 to 85°C. Suitable current densities are in the range from 400 to 4000 A/m² and suitable voltages are in the range from 2.5 to 6 volt.  

[0031] It has been found in the electrolysis that sulfur is reduced preferentially over cathodic splitting of water into hydrogen and hydroxide anions, so that the mixture leaving the cathode space comprises alkali metal cations and essentially (poly)sulfide anions which on concentration and removal of the solvent form alkali metal (poly)sulfide.  

[0032] The mixture comprising second solvent, alkali metal cations and (poly)sulfide anions and further ionic sulfur compounds which leaves the cathode space is concentrated by removal of the second solvent in step (b). Preference is given here to concentration of the mixture comprising second solvent, alkali metal cations and (poly)sulfide anions and further ionic sulfur compounds which is taken off from the cathode space being carried out in an evaporator.  

[0033] The evaporator can be operated continuously or batchwise. Here, any evaporator known to those skilled in the art is suitable for carrying out the concentration operation in step (b). For example, circulation evaporators with natural convection, circulation evaporators with forced circulation, falling film evaporators or thin film evaporators are suitable for continuous evaporation. In the case of batchwise concentration by evaporation, a stirred vessel is particularly suitable. Preference is given, both in continuous evaporation and in batchwise evaporation, to using an evaporator having a condenser.  

[0034] The mixture comprising alkali metal cations, (poly)sulfide anions and further ionic sulfur compounds and second solvent which is led to the evaporator can be preheated before introduction into the evaporator. For this purpose, it is possible to use any apparatus for heating a liquid stream. Preference is given to using a heat exchanger. Heating can be carried out using a heat transfer medium or electrically. Suitable heat transfer media are, for example, thermools, steam or any other heat transfer media known to those skilled in the art.  

[0035] Concentration of the alkali metal cations and (poly)sulfide anions by evaporation is preferably carried out at a temperature in the range from 80 to 400°C, in particular at a temperature in the range from 120 to 350°C and very particularly preferably at a temperature in the range from 150 to 300°C. The pressure of the vapor in the evaporation is preferably in the range from 0.1 to 2 bar absolute, more preferably in the range from 0.2 to 1 bar absolute, in particular in the range from 0.5 to 1 bar absolute.  

[0036] Heating of the evaporator used can, for example up to 200°C, be carried out using steam. Here, it is firstly possible to convey the steam through a pipe in an appropriate heat exchanger or to use an apparatus having a double wall. Heating both by means of a pipe conducted through the apparatus and by means of a double wall is also possible. Apart from steam, any other heat transfer medium, for example a thermool or a salt melt, can also be used. Furthermore, the heat necessary for evaporation can be supplied by means of electric heating or direct firing.  

[0037] The evaporation can be carried out in one or more stages. In the case of a multistage evaporation, it is also advantageous for countercurrent vapor recirculation with or without vapor compression to be provided. The multistage evaporation is preferably carried out in a cascaded manner. In the case of cascaded evaporation, the same or different types of evaporator can be used in the individual stages of the evaporator cascade.  

[0038] The evaporation in step (b) forms an overhead stream comprising second solvent and possibly hydrogen sulfide.  

[0039] The bottoms stream obtained in the evaporation comprises sulfur, alkali metal (poly)sulfide and further ionic sulfur compounds and also traces of second solvent and possibly also sodium thiosulfate and sodium hydroxide. The evaporation residue in the preparation of sodium preferably comprises, in terms of elemental analysis, from 65 to 75% by weight of sulfur, from 20 to 25% by weight of sodium and from 4 to 10% by weight of oxygen, for example a proportion of 69% by weight of sulfur, 23% by weight of sodium and 8% by weight of oxygen.  

[0040] In the preparation of potassium, the evaporation residue comprises, in terms of elemental analysis, for example from 60 to 70% by weight of sulfur, from 25 to 37% by weight of potassium and from 4 to 10% by weight of oxygen.  

[0041] After concentration of the mixture comprising second solvent, alkali metal cations, further ionic sulfur compounds and (poly)sulfide anions by evaporation in step (b), the concentrated mixture obtained as bottoms stream in the evaporation can, in a preferred embodiment, be purified to remove the ionic sulfur-oxygen compounds comprised therein before carrying out the second electrolysis in step (c).  

[0042] To carry out the purification, preference is given to bringing the bottoms stream from step (b) into contact with a gaseous stream comprising hydrogen sulfide. The hydrogen sulfide used for purification is preferably technical-grade hydrogen sulfide. In addition to the hydrogen sulfide, the gas stream fed in can also comprise gases which are inert in the process. Examples of gases which are inert in the process and can be comprised are nitrogen, hydrogen or noble gases, in particular nitrogen.  

[0043] In the purification, alkali metal hydroxide, for example, still comprised in the bottoms stream reacts with the hydrogen sulfide to form alkali metal (poly)sulfide and water. At the same time, second solvent still comprised or water formed in the reaction is removed from the mixture so that essentially impurity-free alkali metal (poly)sulfide is formed.  

[0044] To carry out the purification, the concentrated mixture from (b) and the gaseous stream comprising hydrogen sulfide are preferably conveyed in countercurrent. Here, particular preference is given to using a column, with the concentrated mixture from step (b) being fed in at the top of the column and the gaseous stream comprising hydrogen sulfide being fed in via a side inlet. The hydrogen sulfide ascends in the column and the concentrated mixture from step (b) runs downward in the column.  

[0045] The column used is preferably a column with internals. Suitable internals are, for example, trays, random packing elements or structured packings.  

[0046] The apparatus in which the purification is carried out, for example the column, is preferably dimensioned so that a residence time of the concentrated mixture from step (b) of from at least 10 s to 30 min, preferably at least 2 min, is achieved.
In a preferred embodiment, the column in which the purification is carried out is additionally heated below the side inlet for the gaseous stream comprising hydrogen sulfide. Heating can be effected, for example, by means of a double wall or a pipe which is installed in the column and through which a heat transfer medium flows. As an alternative, electric heating is also conceivable. Suitable heat transfer media are, for example, steam, thermostats or salt melts.

As a result of the additional heating, hydrogen sulfides formed in the mixture are dissociated into hydrogen sulfide and alkali metal (poly)sulfide. For this purpose, a temperature in the range from 320 to 400°C, preferably in the range from 340 to 350°C, is set in the column by means of the additional heating.

At the bottom of the apparatus for carrying out the purification, a mixture comprising essentially alkali metal (poly)sulfides is obtained. In addition, further impurities in amounts of not more than 0.5% by weight, preferably not more than 0.1% by weight, can be comprised. Such impurities comprise, in particular, alkali metal hydroxide.

At the top of the apparatus for the additional purification, a gas stream comprising second solvent and hydrogen sulfide is obtained. The gaseous stream comprising second solvent and hydrogen sulfide which is taken off from the top of the purification apparatus, in particular the column, is fed to a condenser. In the condenser, the second solvent is condensed out from the stream comprising second solvent and hydrogen sulfide and is taken off. The second solvent condensed out is generally still contaminated with hydrogen sulfide and is preferably fed to the cathode space of the first electrolysis. The gaseous, essentially solvent-free hydrogen sulfide is recirculated to the column.

When a multistage, cascaded evaporation is used in step (b), it is possible to carry out the additional purification in one of the evaporation stages, preferably in the last evaporation stage when the second solvent has been virtually completely removed.

After concentration of the mixture comprising second solvent, alkali metal cations and (poly)sulfide anions in step (b) or the additional purification, the resulting stream comprising alkali metal (poly)sulfide is fed to a second electrolysis.

The second electrolysis is preferably carried out in a second electrolysis cell made up of an anode space and a cathode space which are separated by a solid electrolyte which conducts alkali metal cations. Suitable electrolysis cells for the second electrolysis are, in particular, electrolysis cells whose structure corresponds to the structure of electrolysis cells which can be used in sodium-sulfur batteries.

The solid electrolyte is preferably a ceramic which conducts alkali metal cations, in particular β-aluminum oxide, β'-aluminum oxide or β/β'-aluminum oxide. Alkali metal cations of the alkali metal to be prepared are in each case bound in the ceramics.

Apart from the alkali metal β-aluminum oxide, alkali metal β'-aluminum oxide or alkali metal β/β'-aluminum oxide, corresponding alkali metal analogues of NASICON® ceramics are also suitable. The alkali metal used is in each case the alkali metal which is to be isolated by means of the process of the invention.

When the alkali metal which is to be prepared is lithium, NASICONs and particularly preferably Li ion conductors having a garnet structure, for example Li$_2$La$_2$Ta$_2$O$_{12}$ or Li$_2$La$_2$Zr$_2$O$_{12}$, are also suitable.

In the second electrolysis cell, the alkali metal (poly)sulfide melt obtained in the concentration operation in step (b), or the alkali metal (poly)sulfide from the additional purification, is electrochemically separated into alkali metal and sulfur. The electrolysis is carried out at a temperature at which the alkali metal to be prepared is present in molten form. The electrolysis is preferably carried out at a temperature in the range from 290 to 330°C, in particular from 310 to 320°C, under atmospheric pressure.

On the anode side of the electrolysis cell, an electrode composed of a stainless steel stabilized with molybdenum, for example stainless steel having the material number 1.4571, which can be chromium-plated, or an electrode composed of a chromium steel, for example steel having the material number 1.7218, is preferably used. The cathode is preferably an alkali metal electrode. Here, the alkali metal isolated also serves as electrode.

To carry out the second electrolysis, the alkali metal (poly)sulfide is fed in liquid form to the anode space. The alkali metal (poly)sulfide is dissociated into alkali metal cations and (poly)sulfide anions. The alkali metal cations are conducted through the solid electrolyte and thus go into the cathode space. In the cathode space, the alkali metal cations take up electrons and thus form the molten alkali metal. In the anode space, the (poly)sulfide anions release electrons to the anode, so that reduced (poly)sulfides are initially formed and sulfur is ultimately formed. Owing to the temperature of the electrolysis, the sulfur is present in liquid form and can be taken off from the anode space. The sulfur is usually taken off from the upper part of the anode space since sulfur has a lower density than alkali metal (poly)sulfide. The sulfur therefore ascends.

The sulfur obtained in the second electrolysis and unreacted ionic sulfur compounds are, in a particularly preferred embodiment, recirculated to the first electrolysis. For this purpose, the sulfur together with the unreacted ionic sulfur compounds is preferably sprayed in the form of a melt into the suspension fed into the cathode space of the first electrolysis. Here, the melt solidifies and sulfur particles finely dispersed in the second solvent are formed.

Examples of the invention are shown in the figures and are described in more detail in the following description.

In the figures:

FIG. 1 shows a process flow diagram of the first electrolysis,

FIG. 2 shows a process flow diagram of the concentration operation,

FIG. 3 shows a process flow diagram of the additional purification,

FIG. 4 shows a process flow diagram of the second electrolysis,

FIG. 5 shows a process flow diagram of the overall process.

FIG. 6 shows a laboratory electrolysis cell for carrying out the second electrolysis.

In FIG. 1, the first electrolysis is shown in the form of a process flow diagram.

A first electrolysis cell 1 comprises an anode space 3 and a cathode space 5 which are separated from one another by a membrane 7. An anode 9 which is preferably made of coated titanium, with the coating being made up of metal mixed oxides of titanium, tantalum and/or platinum metals such as iridium, ruthenium, platinum and rhodium, is present
in the anode space 3. A cathode 11 which is preferably made of stainless steel is accommodated in the cathode space 5.

[0071] An alkali metal salt solution is fed from a first reservoir 15 via a first feedline 13 to the anode space 3. The alkali metal salt solution comprised in the first reservoir 15 is preferably an aqueous alkali metal halide solution, for example an aqueous alkali metal chloride solution. The alkali metal halide is very particularly preferably sodium chloride.

[0072] The alkali metal salt is preferably dissolved in water as solvent. However, it is also possible to dissolve the alkali metal salt in a suitable organic solvent, for example an alcohol.

[0073] For this purpose, the alkali metal salt is fed via an alkali metal salt line 17 into the first reservoir 15 and the solvent, in particular water, is fed in via a solvent line 19.

[0074] Application of an external voltage closes a current circuit and chlorine is formed at the anode 9 and is taken off together with circulated alkali metal salt solution from the anode space 3.

[0075] In a degassing unit 21, the chlorine is taken off from the stream taken off from the anode space and the remaining stream is recirculated to the first reservoir 15. The chlorine is taken off from the process via a chlorine offtake line 23.

[0076] In the electrolysis cell 1, alkali metal cations pass through the cation-separating membrane 17 into the cathode space 5. A suspension comprising elemental sulfur and second solvent, for example an organic solvent or water, preferably water, flows via a second feedline 25 into the cathode space.

[0077] For this purpose, elemental sulfur is introduced via a sulfur feedline 27 into a second reservoir 31 and second solvent is fed in via a solvent feedline 29 and the two are mixed there. From the second reservoir 31, the mixture comprising second solvent and sulfur is conveyed via the second feedline 25 into the cathode space 5 of the first electrolysis cell. A small amount of alkali metal hydroxide can additionally be added to the mixture comprising second solvent and sulfur in the second reservoir 31 in order to increase the conductivity of the mixture.

[0078] As an alternative to the first reservoir 15 in which solvent and alkali metal salt are mixed and the second reservoir 31 in which elemental sulfur and second solvent are mixed, it is also possible to use any other mixing apparatus known to those skilled in the art. For example, it is also possible to spray the sulfur as a melt into the second solvent and then feed it to the cathode space 5. Furthermore, it is also possible, for example, to meter the alkali metal salt directly into a pipe conveying the solvent.

[0079] A mixture comprising second solvent, alkali metal cations and (poly)sulfide anions is taken off from the cathode space 5 via a cathode discharge line 33. In addition, the mixture taken off via the cathode discharge line 33 can also comprise alkali metal hydroxide. The alkali metal cations and (poly)sulfide anions comprised in the mixture usually form an alkali metal (poly)sulfide.

[0080] In one embodiment, the mixture taken off via the cathode discharge line 33 is circulated and enriched with sulfur and second solvent. For this purpose, it is possible, for example, to firstly recirculate the mixture taken off via the cathode discharge line 33 to the second reservoir 31.

[0081] When no mixture taken off via the cathode discharge line 33 is circulated, the mixture comprising second solvent, alkali metal cations and (poly)sulfide anions which is taken off via the cathode discharge line 33 is fed to a concentration operation. When the mixture taken off via the cathode discharge line 33 is circulated, a substream is taken off and fed to the concentration operation. FIG. 2 shows by way of example a concentration operation by means of evaporation in the form of a flow diagram.

[0082] The stream comprising second solvent, alkali metal cations and (poly)sulfide anions which is taken off as cathode discharge stream 33 is fed to an evaporator 41. The evaporator 41 is, for example, as shown in FIG. 2, a circulation evaporator with natural convection. As an alternative, it is also possible to use a circulation evaporator with forced circulation, a falling film evaporator or a thin film evaporator. Any other evaporators known to those skilled in the art can also be used. When the evaporation is to be carried out batchwise, it is also possible to use, for example, a stirred vessel in place of the circulation evaporator with natural convection depicted here.

[0083] The evaporator 41 is preferably equipped with a liquid precipitator 43.

[0084] When using a circulation evaporator, liquid goes via a circulation line 45 into an evaporator unit 47. The evaporator unit 47 can, for example, be in the form of a shell-and-tube heat exchanger. Here, a heat transfer medium, for example steam, thermoool or a salt melt, flows through the tubes of the shell-and-tube heat exchanger. In addition or as an alternative, the evaporator unit 47 can have a double wall for heating. Furthermore, it is also possible for heating to be carried out electrically or by means of direct firing instead of heating by means of a heat transfer medium. An overhead stream comprising gaseous second solvent, liquid second solvent, alkali metal cations and (poly)sulfide anions is taken off at the top of the evaporator unit 47 and fed to the liquid precipitator 43. In the liquid precipitator 43, the gaseous second solvent is separated off and taken off from the process via a solvent offtake line 49. The mixture comprising second solvent, alkali metal cations and (poly)sulfide anions is circulated until the desired concentration of residual solvent is obtained. As soon as a steady state is reached, mixture comprising second solvent, alkali metal cations and (poly)sulfide anions is uniformly fed into the cathode discharge line 33 opening into the circulation line 45 and before introduction of the mixture from the circulation line, the concentrated mixture comprising second solvent and alkali metal (poly)sulfide is taken off via an offtake line 51.

[0085] In a preferred embodiment, the mixture taken off via the offtake line 51 is purified further. The purification is shown schematically in FIG. 3 with the aid of a flow diagram.

[0086] The concentrated alkali metal (poly)sulfide melt is optionally fed to a preheater 53 and heated in this. Preheating can, for example, be carried out electrically, by means of a heat transfer medium, for example steam, a thermoool or a salt melt. The preheated alkali metal (poly)sulfide melt is then preferably fed into the upper region of a column 55. The column 55 generally comprises internals, for example trays, random packing elements or structured or unstructured packing.

[0087] In the lower region of the column 55, hydrogen sulfide is introduced via a side feedline 57. The hydrogen sulfide can additionally be mixed with an inert gas, for example nitrogen. In the interior of the column 55, the hydrogen sulfide and the alkali metal (poly)sulfide melt are preferably conveyed in countercurrent and intensively mixed. As a
result, any alkali metal hydroxide still comprised in the alkali metal (poly)sulfide melt is converted into alkali metal (poly)sulfide and water.

[0088] An overhead stream 59 comprising water and hydrogen sulfide is taken off at the top of the column 55. The overhead stream 59 is introduced into a condenser 61 in which the water is condensed out. The remaining hydrogen sulfide present in gaseous form is conveyed via a circulation line 63 back to the column 55. The water, which may still comprise residuals of hydrogen sulfide, is taken off from the condenser 61 and, if water is used as second solvent, recirculated via an offtake line 65 to the cathode space of the first electrolysis.

[0089] A stream 67 which comprises essentially solvent-free alkali metal (poly)sulfide is taken off at the bottom of the column 55.

[0090] The alkali metal (poly)sulfide melt obtained in the evaporation or the stream 67 comprising alkali metal (poly)sulfide which is obtained when carrying out the work-up as shown in FIG. 3 is fed to a second electrolysis. This is shown by way of example in FIG. 4.

[0091] The second electrolysis can be carried out in a plurality of stages. For this purpose, a plurality of electrolysis cells 71 are connected in parallel.

[0092] The electrolysis cells 71 each have an anode space 73 in which a plurality of electrode units 75 are installed in the embodiment depicted here. The electrode units 75 each comprise a cylindrical body composed of a solid electrolyte and thus separate a cathode space located in the interior of the solid electrolyte from the anode space 73. The alkali metal (poly)sulfide melt from the evaporation shown in FIG. 2 or, when a further purification is carried out, the alkali metal (poly)sulfide from the purification shown in FIG. 3 is fed via a feedline 79 to the anode space 73 of the respective electrolysis cells.

[0093] During operation of the electrolysis cells 71, the alkali metal (poly)sulfide is dissociated electrochemically into alkali metal and sulfur. Here, alkali metal cations pass through the solid electrolyte which conducts alkali metal cations into the cathode space in which alkali metal is formed. The alkali metal is taken off from the cathode space and discharged via a product line 77. At the same time, sulfur is formed from the polysulfide at the anode. The electrolysis is operated at a temperature at which the alkali metal is present in liquid form.

[0094] For this purpose, a stainless steel electrode is preferably accommodated in the anode space. The sulfur formed rises since it has a lower density than the alkali metal (poly)sulfide. The sulfur can then be taken off via a sulfur offtake line 81 at the upper part of the anode space 73. The sulfur taken off via the sulfur offtake line 81 is preferably recirculated to the first electrolysis shown in FIG. 1. For this purpose, the sulfur is, for example, conveyed via the sulfur feedline 27 to the second reservoir 31. As an alternative, it is also possible, as described above, to spray the sulfur taken off as sulfur melt from the second electrolysis into the second solvent and then feed it to the first electrolysis cell 1.

[0095] The overall process without the additional purification shown in FIG. 3 is shown by way of example in FIG. 5.

[0096] When sodium is to be prepared by the process of the invention, sodium chloride is introduced via the alkali metal salt feedline 17 and preferably water is introduced via the solvent feedline 19; the sodium chloride is dissolved in the water and introduced via the first feedline 13 into the electrolysis cell. In the first electrolysis cell 1, the sodium chloride is separated into sodium ions and chlorine. The chlorine is taken off together with circulating sodium chloride solution from the anode space of the first electrolysis cell 1. The chlorine is separated off and removed from the process via the chlorine offtake line 23. The remaining sodium chloride solution is concentrated by addition of additional sodium chloride and conveyed back into the anode space of the first electrolysis cell 1.

[0097] The sodium ions pass through the cation-permeable membrane 7 and go into the cathode space 5. A mixture comprising solvent, preferably water, and sulfur flows through the cathode space 5. Since sulfur is reduced preferentially over hydrogen, sodium (poly)sulfide is formed in the cathode space and the sodium (poly)sulfide is dissociated into sodium cations and (poly)sulfide anions. The solution comprising sodium (poly)sulfide is fed from the cathode space to the evaporator 41. In the evaporator 41, the sodium (poly)sulfide is concentrated by evaporation of the water. The concentrated sodium (poly)sulfide is subsequently sent to the second electrolysis cells 71 in which the sodium (poly)sulfide is electrolytically dissociated into sodium and sulfur. The sodium ions pass through the solid electrolyte which conducts sodium ions and go into the cathode space from which the sodium formed there is taken off in molten form. Sulfur is taken off from the anode space and recirculated to the first electrolysis.

EXAMPLE

[0098] First Electrolysis Stage:

[0099] The electrolysis of the aqueous sodium chloride solution was carried out in the electrolysis cell shown in FIG. 1. The electrolysis cell was divided by means of a cation-exchanging membrane (Nafion® 324) into an anode space and a cathode space. As anode, use was made of an Ru/Re-titanium mixed oxide-coated titanium anode in the form of expanded metal. The cathode was stainless steel expanded metal having the material number 1.4571.

[0100] The electrolysis was carried out batchwise with stepwise introduction of further sodium chloride. The anolyte was circulated by pumping from the first reservoir 15 through the anode space 3 of the electrolysis cell by means of a laboratory centrifugal pump. At the beginning, 1700 g of a 2.5% strength aqueous sodium tetra-sulfide solution were placed in the cell as anolyte.

[0101] The catholyte was circulated by pumping from the second reservoir 31 through the cathode space 5 of the electrolysis cell by means of a laboratory centrifugal pump. At the beginning, 1566 g of a 23% strength aqueous sodium chloride solution were placed in the cell as catholyte. 80 g of sulfur powder were added to this solution.

[0102] The electrolysis was carried out at a temperature in the range from 75° C. to 80° C., a current density of 2000 A/m² and a cell voltage in the range from 3.5 to 5 volt.

[0103] The electrolysis was carried out batchwise in 4 stages of 40 Ah each, so that a total of 160 Ah were introduced into the cell. After the first electrolysis stage with 40 Ah, 85 g of sodium chloride were added to the anolyte and 80 g of sulfur were added to the catholyte. This was carried out a total of 3 times, so that a total of 320 g of sulfur and 225 g of sodium chloride were added.
During the electrolysis, the anode side was flushed with nitrogen. The anode-side offgas went through two scrubbers which were operated using 10% strength aqueous NaOH and were connected in series.

The cathode side was likewise flushed with nitrogen. The cathode-side offgas was passed through a gas analysis instrument which determined the hydrogen content. The solutions were discharged after the electrolysis and subjected to elemental analysis.

Analytical Results:

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anolyte discharged</td>
<td>864 g</td>
</tr>
<tr>
<td>Chloride</td>
<td>13.9% by weight</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.01% by weight</td>
</tr>
<tr>
<td>Sodium ion</td>
<td>2.9% by weight</td>
</tr>
<tr>
<td>Catholyte discharged</td>
<td>2294 g</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.08% by weight</td>
</tr>
<tr>
<td>Sulfur</td>
<td>15.2% by weight</td>
</tr>
<tr>
<td>Sodium ion</td>
<td>6.5% by weight</td>
</tr>
</tbody>
</table>

175 g of chloride were found in the two scrubbers for the anode offgas.

Concentration:

The cathode output was evaporated batchwise in an electrically heated distillation flask at increasing temperature while stirring. The boiling temperature increased from 102° C. to 200° C. during the concentration operation. The evaporation system was limited at 200° C. The contents of the distillation flask remained liquid over the course of the concentration operation. The distillation was stopped when no more distillate went over.

1684 g of vapor condensate were obtained. The contents of the flask were then cooled to room temperature, resulting in the contents solidifying. The solidified sodium (poly)sulfide melt was crushed in a glove box made inert by means of nitrogen, giving a sodium (poly)sulfide powder. A partial amount of this sodium (poly)sulfide powder was subjected to quantitative elemental analysis.

Analytical Results:

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catholyte concentrate discharged</td>
<td>404.4 g</td>
</tr>
<tr>
<td>Oxygen</td>
<td>10.4% by weight</td>
</tr>
<tr>
<td>Sulfur</td>
<td>59.0% by weight</td>
</tr>
<tr>
<td>Sodium</td>
<td>28.4% by weight</td>
</tr>
</tbody>
</table>

Second Electrolysis Stage:

The electrolysis of the sodium (poly)sulfide melt was carried out in the laboratory apparatus shown in FIG. 6, which was provided with electric heating 101 and a steel housing 100. The electrolysis cell 90 was a U-tube made of borosilicate glass, with the two electrodes together with the ceramic membrane being arranged in an electrolysis leg 91 while the second leg 92 remained without internals. The membrane 93 was a beta"-Al₂O₃ ceramic which conducted sodium ions. The membrane 93 had the form of a tube closed at one end, with sodium 94 being kept within the tube and the sodium (poly)sulfide melt 95 being kept outside the tube. The usable surface of the tubular membrane 93 was 14 cm². As anode 96, use was made of a graphite felt type GF505EA (from SOL) which was connected electrically to the plus side of the power supply via 4 contact plates 97 made of chrome-plated steel having the material number 1.4404. The molten sodium 94 which was electrically connected via a stainless steel rod 98 to the minus side of the power supply served as cathode. Both electrolysis chambers were made inert by means of nitrogen.

The electrolysis was carried out batchwise. Before commencence of the electrolysis, 40 g of the sodium (poly) sulfide powder obtained in the glove box after concentration were introduced into the free leg 92 of the U-tube. The filling opening 99 was then closed. The electrolysis apparatus was then heated from room temperature to 300° C. over a period of 10 hours. This resulted in the sodium (poly)sulfide powder melting. This melt was transferred to the electrolysis zone by means of application of slightly superatmospheric pressure to the free leg.

The electrolysis was carried out at a temperature in the range from 290° C. to 310° C., a current of 1.4 A and a cell voltage in the range from 2.5 to 3 volt over an electrolysis time of 7 h. After the electrolysis, 8 g of sodium metal were discharged.

LIST OF REFERENCE NUMERALS:

1 first electrolysis cell
3 anode space
5 cathode space
7 membrane
9 anode
11 cathode
13 first feedstream
15 first reservoir
17 alkali metal salt line
19 solvent line
21 degassing unit
23 chlorine offtake line
25 second feedstream
27 sulfur feedline
29 solvent feedline
31 second reservoir
33 cathode discharge stream
41 evaporator
43 liquid precipitator
45 circulation line
47 evaporator unit
49 solvent offtake line
51 offtake line
53 preheater
55 column
57 side inlet
59 overhead stream
61 condenser
63 circulation line
65 offtake line
67 stream comprising essentially alkali metal (poly) sulfide
71 second electrolysis cell
73 anode space
75 electrode unit
77 product line
79 feedline
81 sulfur discharge line
90 electrolysis cell
91 electrolysis leg
92 free leg
93 membrane
15. A process for preparing an alkali metal from a salt of the alkali metal which is soluble in a solvent, said process comprising

(a) carrying out a first electrolysis in a first electrolysis cell comprising an anode space and a cathode space, where the anode space and the cathode space of the first electrolysis cell are separated by a membrane which is permeable to alkali metal cations, wherein the salt of the alkali metal dissolved in a first solvent is fed to the anode space and a suspension comprising sulfur and a second solvent is fed to the cathode space, and wherein a mixture comprising the second solvent, the alkali metal cations, (poly)sulfide anions, and further ionic sulfur compounds, is taken off from the cathode space,

(b) concentrating the mixture comprising the second solvent, the alkali metal cations, the (poly)sulfide anions, and the further ionic sulfur compounds, which is taken off from the cathode space, to give a largely solvent-free alkali metal (poly)sulfide melt,

(c) carrying out a second electrolysis at a temperature above the melting point of the alkali metal in a second electrolysis cell comprising an anode space and a cathode space, where the anode space and the cathode space of the second electrolysis cell are separated by a solid electrolyte which conducts alkali metal cations, and wherein the alkali metal (poly)sulfide melt from step (b) is fed to the anode space and sulfur is taken off from the anode space and liquid alkali metal is taken off from the cathode space.

16. The process of claim 15, wherein concentration of the alkali metal cations and the (poly)sulfide anions in the mixture comprising the second solvent, the alkali metal cations, the (poly)sulfide anions, and the further ionic sulfur compounds, which is taken off from the cathode space of the first electrolysis cell, is carried out in an evaporator.

17. The process of claim 15, wherein the concentrating step is carried out at a temperature in the range from 80 to 400°C, and a pressure of the vapor in the range from 0.1 to 2 bar absolute.

18. The process of claim 15, wherein the concentrated mixture obtained in step (b) is purified before carrying out the second electrolysis.

19. The process of claim 15, wherein the concentrated mixture obtained in step (b) is brought into contact with a gaseous stream comprising hydrogen sulfide to effect purification.

20. The process of claim 19, wherein the concentrated mixture obtained in step (b) and the gaseous stream comprising hydrogen sulfide are conveyed in counter-current.

21. The process of claim 19, wherein the purification is carried out in a column, and wherein the concentrated mixture obtained in step (b) is fed in at the top of the column and the gaseous stream comprising hydrogen sulfide is fed in via a side inlet.

22. The process of claim 21, wherein the column is heated below the side inlet for the gaseous stream comprising hydrogen sulfide.

23. The process of claim 15, wherein the solid electrolyte which conducts alkali metal cations of the second electrolysis cell comprises alkali metal β-aluminum oxide, alkali metal β*-aluminum oxide or alkali metal β/β*-aluminum oxide.

24. The process of claim 15, wherein the sulfur taken off from the anode space of the second electrolysis cell is recirculated to the first electrolysis in step (a).

25. The process of claim 15, wherein the alkali metal is sodium, potassium, or lithium.

26. The process of claim 15, wherein the salt of the alkali metal is an alkali metal halide.

27. The process of claim 15, wherein the salt of the alkali metal is sodium chloride.

28. The process of claim 15, wherein the first solvent and/or the second solvent is water.